Onsager symmetry from mesoscopic time reversibility and the hydrodynamic dispersion tensor for coarse-grained systems

Eirik G. Flekkøy[*]
Department of Physics, University of Oslo, P.O. Box 1043 Blindern, 0316 Oslo, Norway

Steven R. Pride[†]
Lawrence Berkeley National Laboratory, Earth Science Division, 1 Cyclotron Road, MS 90-1116, Berkeley, California 94720, USA

Renaud Toussaint[‡]
Institut de Physique du Globe de Strasbourg, University of Strasbourg/EOST, CNRS, 5 rue Descartes, F-67084 Strasbourg Cedex, France
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Onsager reciprocity relations derive from the fundamental time reversibility of the underlying microscopic equations of motion. This gives rise to a large set of symmetric cross-coupling phenomena. We here demonstrate that different reciprocity relations may arise from the notion of mesoscopic time reversibility, i.e., reversibility of intrinsically coarse-grained equations of motion. We use Brownian dynamics as an example of such a dynamical description and show how it gives rise to reciprocity in the hydrodynamic dispersion tensor as long as the background flow velocity is reversed as well.

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I. INTRODUCTION

Onsager reciprocity or symmetry relations [1,2] describe a wide range of cross-coupling phenomena. Even though they were most intensely studied in the 1940s to 1960s—see Ref. [3] for an excellent review—their relevance is still strong in many fields, and they play the role as a foundation of irreversible thermodynamics [4]. Well studied cross-coupling phenomena include the thermomechanical effect (piezoelectrical elements), the thermoelectric effect, electrokinetic phenomena, multispecies molecular diffusion, transference in electrolytic solutions, and thermomagnetism [3]. More recently, the statistical mechanical arguments of Onsager have also been applied in a hydrodynamic context [5,6].

Historically, the diffusion of heat in anisotropic solids and the symmetry of the thermal conductivity tensor have played a key role. These symmetries were observed as early as 1893 by Soret [7,8] and, at the time, partly explained by geometrical arguments pertaining to the symmetries of crystal lattices. But only with the general theory of Onsager, who also used heat diffusion as a starting point, were the wide range of cross-coupling phenomena given a common and fundamental theoretical basis.

Classical Onsager theory as given by de Groot [4] and by Onsager himself is based on the notion of the fundamental time reversibility of the underlying microdynamics. The time-reversal symmetry is attributed to the microscopic equations that describe individual particles. In this paper we demonstrate that the time-reversal symmetry does not have to be attributed to the microdynamics but may just as well be attributed to a mesoscopic description in between the microlevel and that of the linear laws with its transport coefficients and in this case too Onsager reciprocity relations for the macroscale transport coefficients results. This enlarges the scope of irreversible thermodynamics by opening for the application of the same analysis to new systems, and therefore the class of reciprocity relations that results will also be enlarged.

This is exemplified here by a case of flow of two miscible fluids in a complex medium. This flow is described by a hydrodynamic dispersion tensor which becomes symmetric under hydrodynamic flow reversal by virtue of Onsager reciprocity. This is shown by a mesoscopic approach where Brownian dynamics is taken as the mesoscopic and lowest level description. The Brownian particles are simply random walkers that move along on the hydrodynamic background field $\mathbf{u}$. This means that we are dealing with three separate length scales:

(i) the mean free path of the particles,

(ii) the hydrodynamic scale on which the particle motion may be averaged into velocity and density fields ρ and $\mathbf{u}$, and

(iii) the porous-continuum scale on which averaging over the geometric heterogeneities and flow field of the porous medium makes sense.

These different scales are assumed to be sufficiently far apart.

The end result, which pertains to the porous-continuum scale show that the tensor, relating the concentration gradients in the spatial direction i to the diffusive flux in direction j satisfies the symmetry relation,

$$D_{ij}(\mathbf{u}) = D_{ji}(-\mathbf{u}). \tag{1}$$

In doing so we make contact with the results of Auriault *et al.* [9] who showed these relations, albeit on the basis of continuum mechanics and only in the small Péclet (Pe) number limit.

The structure of the derivation proceeds from the equations of motion of the Brownian particles and the equivalent Fokker-Planck equation. Then a small numerical simulation is used to show that particle number fluctuations behave as in an equilibrium situation, even though our system is not in equilibrium but in a driven steady state. The standard Onsager theory may then be applied as soon as the fluxes and forces

[*]flekkoy@fys.uio.no
[†]srpride@lbl.gov
[‡]renaud.toussaint@unistra.fr

governing the entropy production are identified. The Gibbs expression for the entropy [10,11] allows this identification in a straightforward way. The end result of Eq. (1), which belongs on the largest scale, is thus connected to the time reversibility on the smallest scale (i).

II. RECIPROCITY DERIVED FROM THE MESOSCOPIC LEVEL

The link between the microscopic reversibility and the reciprocity of the transport coefficients is the regression hypothesis, which expresses the idea that spontaneous fluctuations on the average decay according to the macroscopic laws with their transport coefficients. This very plausible hypothesis may also be proved through the fluctuation-dissipation theorem on the basis of Hamiltonian dynamics [12,13].

However, given this hypothesis, any reversible microdynamics will suffice as a basis for Onsager reciprocity. This includes equations of motions which are normally regarded as mesoscopic in nature, i.e., an averaged representation of collections of particles. The Brownian dynamics consists of a number of mesoscopic particles, labeled n, that are propagated by simple random shifts to their velocities. Each particle velocity is given by a prescribed random update along with a background velocity field $\mathbf{u}(\mathbf{x})$. So, adding the random component $\delta\mathbf{v}_n$, the particle velocity becomes

$$\dot{\mathbf{r}}_k = \mathbf{u}(\mathbf{r}_k) + \delta\mathbf{v}_k. \tag{2}$$

Here $\delta\mathbf{v}_k$ is picked from a symmetric distribution $p(\delta\mathbf{v}_k) = p(-\delta\mathbf{v}_k)$. Note that Eq. (2) may also be written as

$$d\mathbf{r}_k = \mathbf{u}(\mathbf{r}_k)dt + d\mathbf{W}, \tag{3}$$

where $d\mathbf{W}$ is a Wiener process $\langle dW_i dW_j\rangle = \sigma^2\delta_{ij}dt$ where the steps dW_i are uncorrelated and sampled from a Gaussian distribution.

The above equation may be derived as the overdamped inertialess limit of the Langevin equation. This equation, which describes the balance of dissipative and fluctuating forces is mesoscopic and probabilistic in nature. It is in itself not invariant under time reversal. But Eq. (2), which is also mesoscopic and probabilistic in nature, is.

Time-reversal $t \to -t$ implies $\partial/\partial t \to -\partial/\partial t$ and $\dot{\mathbf{r}}_k \to -\dot{\mathbf{r}}_k$ as well as $\delta\mathbf{v}_k \to -\delta\mathbf{v}_k$. So, if we combine time reversal with the reversal of the background field $\mathbf{u}(\mathbf{x}) \to -\mathbf{u}(\mathbf{x})$, Eq. (2) is left invariant. Note that we rely on the symmetric form of the $p(\delta\mathbf{v})$ distribution. If solid boundaries are present, as in a porous medium, their impermeable nature may be represented by the time-reversible prescription $d\mathbf{r}_k \to -d\mathbf{r}_k$ at the walls. This means that a time-sequence $\mathbf{r}_k(t)$ with the background field $\mathbf{u}(\mathbf{x})$ will be statistically indistinguishable from the reverse time-sequence $\mathbf{r}_k(-t)$ with the background field $-\mathbf{u}(\mathbf{x})$ as is illustrated in Fig. 1. Correspondingly, any function of a set of forward time sequences $\{\mathbf{r}_k(t)\}_{\mathbf{u}}$ associated with the background field $\mathbf{u}(\mathbf{x})$ will be statistically invariant if we make the replacement $\{\mathbf{r}_k(t)\}_{\mathbf{u}} \to \{\mathbf{r}_k(-t)\}_{-\mathbf{u}}$.

An immediate consequence of this is that any macroscopic variables $N_i(t)$ that are functions of the particle positions $\{\mathbf{r}_k\}$ only will have an autocorrelation function that satisfies

$$\langle N_j(\tau)N_k(0)\rangle_{\mathbf{u}} = \langle N_j(-\tau)N_k(0)\rangle_{-\mathbf{u}}, \tag{4}$$

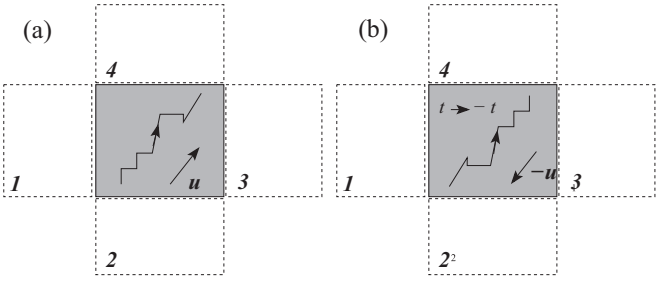

FIG. 1. The effect of time reversal with the implied $\mathbf{u} \to -\mathbf{u}$ inversion in a porous medium (shaded). The forward time path in (a) is inverted in (b).

where the average $\langle\cdots\rangle_{\mathbf{u}}$ and $\langle\cdots\rangle_{-\mathbf{u}}$ denote ensemble averages with background fields $\pm\mathbf{u}$. In order to define boundary conditions for the flow while maintaining a total system which is closed, we introduce reservoirs surrounding the porous medium. In these reservoirs $\mathbf{u} = 0$. We will take N_i to be the particle number in one of these surrounding reservoirs, labeled by i and shown in Fig. 1.

Since Eq. (4) is the basic starting point in the proof of the Onsager reciprocity relations [4], it may be shown that the linear laws relating the time evolution of the N_i's with the corresponding forces will be defined by coefficients that are reciprocal.

The flow reversal $\mathbf{u} \to -\mathbf{u}$ is feasible whenever the Reynolds number is small. The resulting steady states may be studied directly by computer simulation techniques, which are well established now but were unknown at the time when Onsager's reciprocity relations were established experimentally [3].

III. THE FOKKER-PLANCK EQUATION AND THE CONTINUUM DESCRIPTION

Since there is no conservation of momentum as in Hamiltonian dynamics, our phase space consists of the N particle positions only, i.e., $\Gamma = \{\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N\}$. Following standard procedures [14] the Fokker-Planck equation, which describes the distribution $\Psi(\Gamma,t)$ in this phase space, may be derived by the requirement that the linear procedures of taking the time derivative and the average should commute. This should be the case for any function $f(\Gamma)$ so that $\langle df/dt\rangle = d\langle f\rangle/dt$ or

$$\int d\Gamma \frac{\partial\Psi}{\partial t}dt\, f(\Gamma) = \int d\Gamma\, \Psi(\Gamma,t)df(\Gamma). \tag{5}$$

Using Eq. (3), the right hand side becomes

$$\begin{aligned}
&\int d\Gamma\, \Psi(\Gamma,t)df(\Gamma)\\
&= \int d\Gamma\, \Psi\left(\frac{\partial f}{\partial \mathbf{r}_k}\cdot\dot{\mathbf{r}}_k dt + \frac{1}{2}\frac{\partial^2 f}{\partial\mathbf{r}_j\partial\mathbf{r}_k}dW_k dW_j\right)\\
&= \int d\Gamma\, \Psi(\Gamma,t)\left(\mathbf{u}_k\cdot\frac{\partial f}{\partial\mathbf{r}_k} + \frac{\sigma^2}{2}\nabla_k^2 f\right)dt\\
&= \int d\Gamma\, f(\Gamma)\left(-\nabla_k\cdot(\Psi\mathbf{u}_k) + \frac{\sigma^2}{2}\nabla_k^2\Psi\right)dt,
\end{aligned} \tag{6}$$

where a summation over repeated indices is assumed here and throughout. In going from the second to the third line above, Itô's lemma was applied, and in going to the fourth line, partial integration was applied. Comparing with Eq. (5) we get the Fokker-Planck equation,

$$\frac{\partial \Psi}{\partial t} = -\nabla_k \cdot [\Psi(\Gamma,t)\mathbf{u}_k] + \frac{\sigma^2}{2}\nabla_k^2 \Psi(\Gamma,t). \tag{7}$$

Since this equation is in the form $\partial\Psi/\partial t = -\nabla_k \cdot \mathbf{J}_k$, it may also be considered a Liouville equation that expresses the local conservation of system numbers in the ensemble. It is easily observed that Eq. (7) allows the product solution,

$$\Psi(\Gamma,t) = \prod_{k=1}^{N} [\Delta V\ P(\mathbf{r}_k,t)], \tag{8}$$

where ΔV^N is the elementary subvolume that is used to discretize phase space and the single particle probability distribution satisfies the advection-diffusion equation,

$$\frac{\partial P}{\partial t} = -\nabla \cdot (P\mathbf{u}) + D\nabla^2 P, \tag{9}$$

where $D = \sigma^2/2$. As the particle density is simply $\rho = NP$, this may be written

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho\mathbf{u}) + D\nabla^2 \rho, \tag{10}$$

which is indeed the hydrodynamic description on scale (ii) required to govern the upscaled flow and dispersion.

IV. GIBBS ENTROPY AND THE ENTROPY PRODUCTION

We will calculate the entropy by a standard Gibbs expression,

$$S = -k_B \sum_{\Gamma} \Psi(\Gamma,t) \ln\ \Psi(\Gamma,t), \tag{11}$$

where we also allow for a time dependence. This expression was applied by Seifert [10] and Speck *et al.* [11] who used it to introduce the entropy of single paths and expanded the description to include the energy exchange between the Brownian particle system and the system of the embedding fluid (the solvent). In doing this, energy conservation and exchange between the two systems are natural and physical assumptions. For our purposes, however, we only need to consider the system of Brownian particles, and in focusing the description on a subsystem only, we cannot assume energy conservation. For this reason, thermal diffusion is not part of the picture either.

Replacing the above sum by an integral,

$$\sum_{\Gamma} = \prod_k \frac{\int d^3 r_k}{\Delta V}, \tag{12}$$

and using Eq. (8), the entropy becomes

$$\begin{aligned} S &= -k_B \prod_k \int d^3 r_k P(\mathbf{r}_k,t) \ln \left(\prod_{k'} [P(\mathbf{r}_{k'},t)\Delta V] \right) \\ &= -k_B \prod_k \int d^3 r_k P(\mathbf{r}_k,t) \sum_{k'} \ln[P(\mathbf{r}_{k'},t)\Delta V] \\ &= -k_B \sum_{k'} \int d^3 r_{k'} P(\mathbf{r}_{k'},t) \ln[P(\mathbf{r}_{k'},t)\Delta V] \\ &= -k_B \int d^3 x\ \rho(\mathbf{x},t) \ln \left(\rho(\mathbf{x},t) \frac{\Delta V}{N_{\rm tot}} \right). \end{aligned} \tag{13}$$

In going from the first to the second line we have taken the product out from inside the ln function, and in going from the second to the third line we have used that all $k \neq k'$ integrals only produce a factor of 1 due to the normalization of $P(\mathbf{r}_k,t)$ and in passing to the last, the fact that the summand is k independent and the $\rho = PN_{\rm tot}$ relation again. We will write the entropy as

$$S = \int d^3 x\ s(\mathbf{x},t), \tag{14}$$

where the entropy density,

$$s(\mathbf{x},t) = -k_B \rho\ \ln \left(\frac{\rho}{\rho_m} \right), \tag{15}$$

and the upper limit for the density $\rho_m = N_{\rm tot}/\Delta V$ would result from putting all particles in one cell.

A. Numerical evidence for equilibrium distributions in the steady states

In order to apply Onsager theory it is standard to start out with the assumption that every microstate is equally probable and use this to express the relevant probability distributions in terms of the entropy. Unfortunately, the standard assumption of local equilibrium [15] may not prove this assumption in a rigorous way as small local deviations from equilibrium may in principle add up to create a finite effect on, say, the particle number in a reservoir.

The standard equilibrium result for the probability distribution in a closed system is that $P(N_i) \propto \exp[S(N_i)/k_B]$. However, in our case, the system is not in equilibrium, and the particle numbers N_i depend on $\mathbf{u}$ through the steady state solution of our Fokker-Planck equation or more directly on Eq. (10). The direct generalization of the equilibrium result is then given by using the entropy of Eq. (13). The probability of a given reservoir particle number N_i then takes the form

$$P(N_i,\mathbf{u}) \propto \exp[S(N_i,\mathbf{u})/k_B], \tag{16}$$

where $S(N_i,\mathbf{u})$ is the entropy given by Eq. (13). This relation is a necessary basis for the application of Onsager theory, so we need to show that this equilibrium result holds for our nonequilibrium driven system as well.

Fortunately, it is straightforward to show this numerically. However, in order to do this we need to work out the prediction that results from the combination of Eqs. (13) and (16). If the volume integral of Eq. (13) is discretized into a sum over phase space cells of volume ΔV_α, the total entropy of the central cell and the reservoir, may be written

$$\begin{aligned} \frac{S}{k_B} &= -\sum_\alpha N_\alpha \ln \left(\frac{N_\alpha}{N_{\rm tot}} \right) \\ &= -\sum_\alpha (N_\alpha \ln\ N_\alpha - N_\alpha \ln\ N_{\rm tot}), \end{aligned} \tag{17}$$

where we have introduced the new label α to label the number of particles $N_\alpha = \rho(\mathbf{x}_\alpha)\Delta V_\alpha$ located in ΔV_α. We may further split N_α in an average and a fluctuation $N_\alpha = \overline{N}_\alpha + \delta N_\alpha$, where $\delta N_\alpha \ll \overline{N}_\alpha$ and $\overline{N}_\alpha = \overline{N}_\alpha(\mathbf{x},\mathbf{u})$. Components of S that are δN_α independent, that is, constant terms under variations of the N_α's will disappear under the normalization of $P(N,\mathbf{u})$. We may therefore group any such terms into a constant term S_0''. In particular, the last term above becomes $\sum_\alpha N_\alpha \ln N_{\rm tot} = N_{\rm tot} \ln N_{\rm tot}$. We may then write

$$\begin{aligned}
\frac{S}{k_B} &= -\sum_\alpha N_\alpha \ln N_\alpha + \frac{S_0''}{k_B} \\
&= -\sum_\alpha N_\alpha \ln \overline{N}_\alpha + N_\alpha \ln\left(1 + \frac{\delta N_\alpha}{\overline{N}_\alpha}\right) + \frac{S_0''}{k_B} \\
&\approx -\sum_\alpha \left\{ (\overline{N}_\alpha + \delta N_\alpha) \ln \overline{N}_\alpha + (\overline{N}_\alpha + \delta N_\alpha) \right. \\
&\quad \left. \times \left[\frac{\delta N_\alpha}{\overline{N}_\alpha} - \frac{1}{2}\left(\frac{\delta N_\alpha}{\overline{N}_\alpha}\right)^2 \right] \right\} + \frac{S_0'}{k_B} \\
&= -\sum_\alpha \left\{ \delta N_\alpha \ln \overline{N}_\alpha + (\overline{N}_\alpha + \delta N_\alpha) \right. \\
&\quad \left. \times \left[\frac{\delta N_\alpha}{\overline{N}_\alpha} - \frac{1}{2}\left(\frac{\delta N_\alpha}{\overline{N}_\alpha}\right)^2 \right] \right\} + \frac{S_0}{k_B} \\
&\approx -\sum_\alpha \left(\delta N_\alpha \ln \overline{N}_\alpha + \frac{\delta N_\alpha^2}{2\overline{N}_\alpha} \right) + \frac{S_0}{k_B}, \qquad (18)
\end{aligned}$$

where we have used the facts that $\sum_\alpha \delta N_\alpha = 0$, the S_0'', S_0', and S_0 only differ by δN_α-independent terms, the second order expansion $\ln(1+x) \approx x - x^2/2$, and finally, that we may discard a δN_α^3 term.

The resulting distribution,

$$P(\{N_\alpha\},\mathbf{u}) \propto \prod_\alpha \exp\left(-\frac{\delta N_\alpha^2}{2\overline{N}_\alpha} - \delta N_\alpha \ln \overline{N}_\alpha \right) \qquad (19)$$

factorizes into a simple product of single elementary cell probabilities.

These elementary cells were introduced to discretize phase space and belong on the smallest scale (i), whereas we are in fact interested in the particle populations on the hydrodynamic scale (ii), which take the form

$$N_i = \sum_{\alpha \epsilon m(i)} N_\alpha, \qquad (20)$$

where the notation $\alpha \epsilon m(i)$ is to be understood in the sense that i labels a supercell composed of many elementary cells and $m(i)$ is the set containing the corresponding α values. In the following we will assume that in such a supercell there are M elementary cells of equal size with only negligible variations in $\mathbf{u}(\mathbf{x})$ between them. This assumption resembles the standard assumption of local equilibrium, both in the fact that it assumes negligible variations in the hydrodynamic fields and by the underlying requirement that scales (i) and (ii) are separated. With these two assumptions we can take the $\ln \overline{N}_\alpha$ term to be constant under the local $\alpha \epsilon m(i)$ sum, and Eq. (19) may be written in the following way:

$$\begin{aligned}
P(\{N_i\},\mathbf{u}) &\propto \prod_i \exp\left(-\sum_{\alpha \epsilon m(i)} \frac{\delta N_\alpha^2}{2\overline{N}_\alpha} + \ln \overline{N}_\alpha \delta N_\alpha \right) \\
&= \prod_i \exp\left[\ln \overline{N}_\alpha \delta N_i - \left(\sum_{\alpha \epsilon m(i)} \frac{\delta N_\alpha^2}{2\overline{N}_\alpha} \right) \right]. \qquad (21)
\end{aligned}$$

Here the δN_α^2 term implies that the fluctuations $\delta N_\alpha^2 \sim \overline{N}_\alpha$ so that the sum $\sum_{\alpha \epsilon m(i)} \delta N_\alpha^2/(2\overline{N}_\alpha) \sim M$. On the other hand, the $\delta N_i = \sum_{\alpha \epsilon m(i)} \delta N_\alpha$ term is a sum of M independently fluctuating contributions each with a finite variance and hence, according to the central limit theorem, has a variance $\langle \delta N_i^2 \rangle \sim M$. For this reason the last term in the exponent is $\ln \overline{N}_\alpha \delta N_i \sim \ln \overline{N}_\alpha \sqrt{M}$. Taking $M \gg 1$ we see that this term may be neglected compared to the quadratic term. This gives

$$\begin{aligned}
P(\{N_i\},\mathbf{u}) &\propto \prod_i \exp\left(-\ln \overline{N}_\alpha \delta N_i - \sum_{\alpha \epsilon m(i)} \frac{\delta N_\alpha^2}{2\overline{N}_\alpha} \right) \qquad (22) \\
&\approx \prod_i \exp\left(-\sum_{\alpha \epsilon m(i)} \frac{\delta N_\alpha^2}{2\overline{N}_\alpha} \right). \qquad (23)
\end{aligned}$$

This result has the standard equilibrium form, although it represents a nonequilibrium generalization by virtue of the $\mathbf{u}(\mathbf{x})$ dependence in $\overline{N}_\alpha$. The result of Eq. (23) shows that the δN_i's are distributed *exactly as if* they were the sum of M independent terms, i.e., $\delta N_i = \sum_\alpha \delta N_\alpha$, which independently satisfy a Gaussian distribution of variance $\overline{N}_\alpha$. The central limit theorem then tells us that the δN_i's too are given by a Gaussian distribution with a variance $M\overline{N}_\alpha = \overline{N}_i$, that is,

$$P(\{N_i\},\mathbf{u}) \propto \prod_i \exp\left(-\sum_i \frac{\delta N_i^2}{2\overline{N}_i} \right). \qquad (24)$$

The same argument applies unchanged to further upscaling, so the N_i's in Eq. (24) may also be taken to represent the entire populations of the reservoirs. This means that in the simulations we may use only two volumes, the one where the driving takes place $\mathbf{u}(\mathbf{x}) \neq 0$ and the reservoir where $\mathbf{u}(\mathbf{x}) = 0$. The resulting distribution of the particle number in any given region is insensitive to the internal variations in $\rho(\mathbf{x})$. Due to overall conservation of particles, the two average particle numbers that enter Eq. (19) are $\overline{N}_i$ and $N_{\rm tot} - \overline{N}_i$ (now $i = 1$), and the corresponding distribution is

$$P(N_1) \propto \exp\left[-\delta N_1^2 \left(\frac{1}{2\overline{N}_1} + \frac{1}{2(N_{\rm tot} - \overline{N}_1)} \right) \right], \qquad (25)$$

which narrows to a δ peak as $\overline{N}_1 \to N_{\rm tot}$.

To verify this result numerically we simply simulate the dynamics of 1000 particles that behave according to Eq. (3). Taking the geometry that is illustrated in Fig. 2 as the proving ground we measure the distribution of the number N_1 of particles that reside in the reservoir region. For simplicity there is only one reservoir in this case, and it encloses the gray region, which is the only region with a nonzero background velocity field. Three cases of different velocity fields were studied, and in all the simulations the initial particle

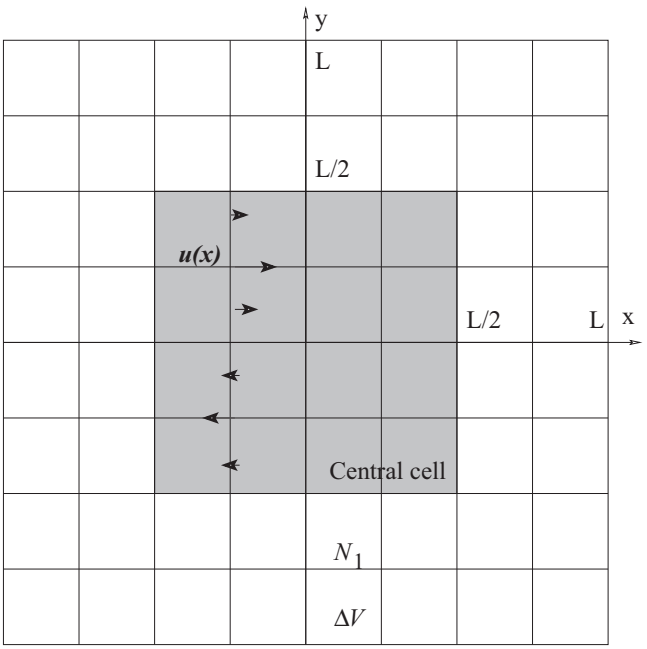

FIG. 2. Illustration of the Brownian dynamics simulation setup. The background velocity $\mathbf{u}(\mathbf{x})$ vanishes outside the central region, and the particle number N_1 outside in the reservoir region is recorded. The subcells have volume ΔV.

distribution was homogeneous. For any particle that arrived outside the reservoir region, the replacement $\delta\mathbf{r}_n \to -\delta\mathbf{r}_n$ was performed. The equilibrium case with $\mathbf{u} = 0$ was verified first before a constant field $u_x = u_0$ and a sinusoidal field $u_x = u_0 \sin(2\pi y/L)$ were studied. In Fig. 3 the constant field is observed to reduce the particle number in the central cell more efficiently than the sinusoidal field as one would expect from the density depletion on the upstream side in the reservoirs.

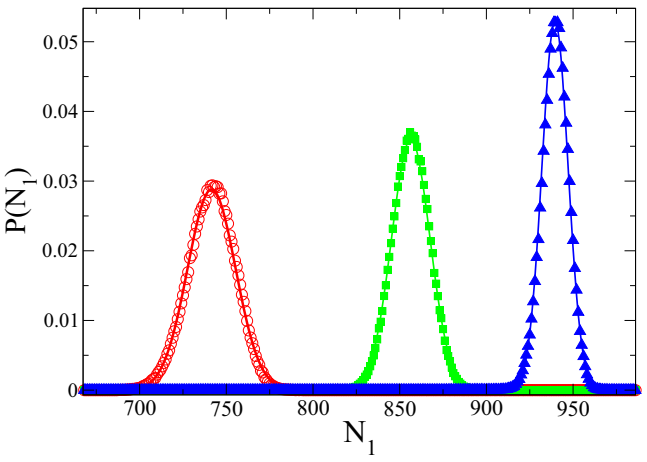

FIG. 3. The distributions $P(N)$ for different flow conditions in the central cell illustrated in Fig. 2. The circles, squares, and triangles show measurements, and the straight lines show the theoretical expectation of Eq. (25). The red circles show the distribution that results from $\mathbf{u} = 0$, the green squares show $u_x = u_0 \sin(2\pi y/L)$, and the blue triangles show $u_x = u_0$, all with a velocity of $u_0 = 1$. The Péclet number is $\mathrm{Pe} = u_0 L/D = 50$ in all cases. The total particle number is 1000, and the average is taken over 400 000 time steps.

In the simulations the driving velocity causes the average particle number in the reservoir to change significantly as is apparent in Fig. 3. The agreement between simulation and theory is good as one would expect. In fact, the $P(N,\mathbf{u})$ distributions adhere quite exactly to the equilibrium prediction. In the following we will base the derivation of the reciprocity relations on our numerical demonstration of Eq. (16).

It is instructive to compare our system with the equilibrium system of a dilute particle suspension in a gravitational or potential field. In steady state, $\partial P/\partial t = 0$, and Eq. (10) expresses the local balance between advective and diffusive currents,

$$\nabla \cdot (\rho\mathbf{u} - D\nabla\rho) = 0. \tag{26}$$

Physically, this local balance is similar to that governing the suspension. However, the situations are indeed different. In fact, for the suspension in a potential field one has a Boltzmann distribution $\rho \propto \exp[-\phi/(k_B T)]$, where ϕ is the potential energy of the Brownian particle and Eq. (26) becomes the basis for proving the Einstein relation [16]. In this case the velocity is not given as a background field but as $\mathbf{u} = -\mu_B \nabla\phi$ where μ_B is the particle mobility. In this case the velocity field is vorticity free. When the Boltzmann distribution is used, Eq. (26) takes the form of the stronger condition $\rho\mathbf{u} - D\nabla\rho = 0$, and particle exchange between two locations A and B will then be in mutual equilibrium—in other words, detailed balance may be assumed. In this case, the standard tools of statistical mechanics are available, and in particular, every microstate may be taken as equally probable in an ensemble of closed systems, and the population probabilities will be given by Eq. (16).

B. Entropy production

The entropy production for any subsystem is obtained by taking the time derivative of Eq. (13) to get

$$\dot{S} = -k \int d^3x \frac{\partial\rho}{\partial t}\left(\ln\frac{\rho\,\Delta V}{N_{\mathrm{tot}}} + 1\right). \tag{27}$$

Then, using Eq. (10) gives

$$\begin{aligned}\dot{S} &= -k_B \int d^3x\, \nabla\cdot(-\rho\mathbf{u} + D\nabla\rho)\left(\ln\frac{\rho\,\Delta V}{N_{\mathrm{tot}}} + 1\right)\\ &= k_B \int d^3x\, \nabla\cdot\left((\rho\mathbf{u} - D\nabla\rho)\ln\frac{\rho\,\Delta V}{N_{\mathrm{tot}}} - D\nabla\rho\right)\\ &\quad + k_B \int d^3x \left(D\frac{(\nabla\rho)^2}{\rho} + \rho\nabla\cdot\mathbf{u}\right),\end{aligned} \tag{28}$$

which may also be written

$$\dot{S} = \int d^3x(\sigma - \nabla\cdot\mathbf{j}_S), \tag{29}$$

with an entropy current,

$$\mathbf{j}_S = s\mathbf{u} + k_B\left[\ln\left(\frac{\rho}{\rho_m}\right) + 1\right]D\nabla\rho, \tag{30}$$

that vanishes on any materially closed surface and an entropy production per unit volume,

$$\sigma = k_B\left(D\frac{(\nabla\rho)^2}{\rho} + \rho\nabla\cdot\mathbf{u}\right). \tag{31}$$

The $\nabla\cdot\mathbf{u}$ term reflects the entropy changes due to the local variations in specific volume for the Brownian particles [15]. Without it the entropy would remain constant under a uniform expansion of the system with $\nabla\rho$ fixed. In fact, if we were to introduce an ideal gas pressure for the particles $p = k_BT/v$, where $v = 1/\rho$ is the volume per particle, it is straightforward to show that $k_BT\rho\nabla\cdot\mathbf{u} = p\,dv/dt$. This means that the compressibility term is nothing but the familiar work term [15]. In our case, where $\mathbf{u}$ is discontinuous across the reservoir boundaries, the $\nabla\cdot\mathbf{u}$ is nonzero only there [17]. Away from the boundaries we may take the flow to be incompressible, and only the bulk term, which we denote σ_0, remains

$$\sigma_0 = k_BD\frac{(\nabla\rho)^2}{\rho}. \tag{32}$$

This expression may be written in a more familiar form by introducing the chemical potential μ. Without energy as a system variable, the Clausius formula is simply

$$T\,dS = -\mu\,dN, \tag{33}$$

and

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_V. \tag{34}$$

So, for the purpose of relating the two intensive thermodynamic quantities ρ and μ we assume for the moment a constant ρ value so that the integral in Eq. (13) becomes a factor V. This gives

$$\mu = k_BT\,\ln\left(\frac{\rho}{\rho_m}\right). \tag{35}$$

Note that, since $\rho_m \gg \rho$, μ must be large and negative. Hence, the addition of a particle will always increase the entropy as it should. Allowing spatial variations again and taking the gradient then gives

$$\frac{\nabla\rho}{\rho} = \frac{\nabla\mu}{k_BT}, \tag{36}$$

which by insertion in Eq. (32) gives

$$\sigma_0 = -\mathbf{j}\cdot\nabla\left(\frac{\mu}{T}\right), \tag{37}$$

where the diffusive current is $\mathbf{j} = -D\nabla\rho$. This simple expression is the familiar form of the entropy production as given by de Groot and Mazur [15] when all work and heat terms that are linked with the conservation of energy are removed. Note that in the above formulas T is a constant, which is proportional to the step size variance σ^2.

V. FROM THE PORE LEVEL TO THE COARSE-GRAINED POROUS-CONTINUUM LEVEL

In order to make contact with the hydrodynamic dispersion tensor, we need to pass from the continuum description of the Brownian particles as given in Eq. (10) to the coarse-grained version of this continuum description [18]. It is only in the coarse-grained version of this theory in a porous medium that the diffusivity becomes a tensor $\mathbf{D}$ with reciprocity relations attached.

The hydrodynamic dispersion tensor $\mathbf{D}$ describes the coarse-grained advection-diffusion flow of solute in a porous media. The medium is divided into cubic cells, centered at $\mathbf{x}$, with an average concentration $\rho_0(\mathbf{x})$, and the porous-continuum particle current is given as

$$\mathbf{J} = \rho_0\overline{\mathbf{U}} - \mathbf{D}\cdot\nabla\rho_0, \tag{38}$$

where $\overline{\mathbf{U}}$ is the cell averaged flow velocity and $\nabla\rho_0$ is defined by the boundary values so that its components are

$$(\nabla\rho_0)_i = \frac{\Delta C_i}{L}, \tag{39}$$

as shown in Fig. 4. The average value $\rho_0(\mathbf{x})$ is centered in the sense that it will always be the average of the face values. The dispersion tensor depends on flow velocity so that $D_{ij} = D_{ij}(\overline{\mathbf{U}})$.

A. Entropy production on the porous-continuum scale

Having derived the entropy production at the hydrodynamic scale (ii), we may now integrate it to the porous-continuum scale. To do so, we first describe the assumptions implicit in Fig. 4. We assume that the central cell is supporting steady state transport in which the entropy irreversibly produced in the transport process is fluxing into the surrounding cells so that in the central cell $\dot{S} = 0$.

This steady state is really a slowly evolving transient where the thermodynamic quantities in the reservoirs change quasistatically. In other words, the flow through the central

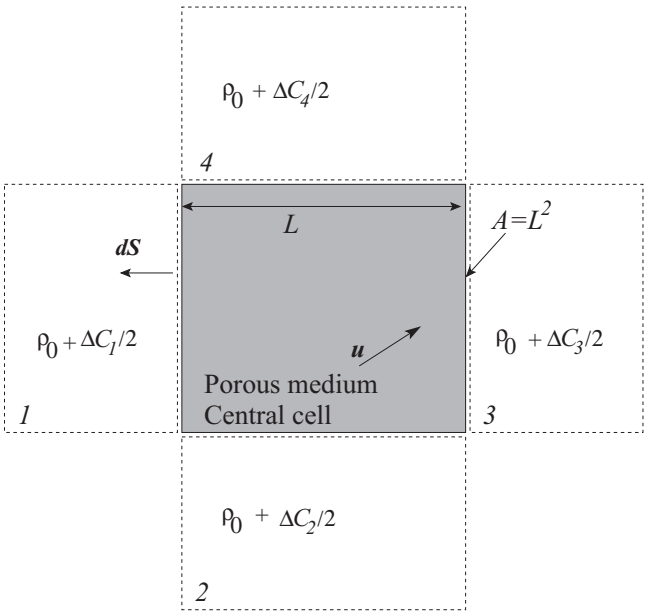

FIG. 4. The porous medium connected to four reservoirs of given constant temperatures and concentration deviations ΔC_i. The reservoirs are assumed to be in equilibrium, the central cell is in the steady state, and the concentration deviations are symmetric in the sense that $\Delta C_{i+2} = -\Delta C_i$.

cell must be slow enough for the reservoirs to remain close to equilibrium. This steady state is thus different from the form of the steady state, which becomes the equilibrium state when $\mathbf{u} = 0$, and where the average values of the thermodynamic quantities no longer change. In the next section we will consider fluctuations around this equilibrium steady state which are linked to the present slow transients by the regression hypothesis.

Since $\dot{S} = 0$ in the central cell, we may integrate Eq. (29) over this cell only and apply Gauss's theorem to get

$$\int d^3x\, \sigma = \int d^3x\, \nabla \cdot \mathbf{j}_S = \int d\mathbf{S} \cdot \mathbf{j}_S, \tag{40}$$

where the surface element $d\mathbf{S}$ points away from the central cell. In addition, we assume the reservoir cells are in quasistatic equilibrium, which means they move through equilibrium states with $\mathbf{u} = 0$ throughout, and the entropy change is given by the Clausius formula Eq. (33). This means that the entropy production may be calculated either by Eq. (40) for the central cell or by the Clausius formula for the reservoirs.

Under these assumptions, we will calculate the total entropy production of the central cell from the surface integral of Eq. (40). The condition that $\mathbf{u} = 0$ at the interface with the reservoir cells means that $\mathbf{j}_S$ of Eq. (30) simplifies and

$$\begin{aligned}\int d\mathbf{S} \cdot \mathbf{j}_S &= k_B D \int d\mathbf{S} \cdot \nabla\rho \left[\ln\left(\frac{\rho}{\rho_m}\right) + 1\right] \\ &= k_B D \int d\mathbf{S} \cdot \nabla\rho\, \ln\, \rho \\ &= -k_B \int d\mathbf{S} \cdot \mathbf{j}\, \ln\, \rho,\end{aligned} \tag{41}$$

where we have also used the fact that by particle conservation in the steady state $\int d\mathbf{S} \cdot D\nabla\rho = 0$.

Now, the number of particles passing across each face of the central cell into the respective reservoir per unit time $\dot{N}_i$ may be written

$$\begin{aligned}\dot{N}_{i+2} &= \int_{x_i=+L/2} d\mathbf{S} \cdot \mathbf{j}, \\ \dot{N}_i &= \int_{x_i=-L/2} d\mathbf{S} \cdot \mathbf{j},\end{aligned} \tag{42}$$

where the partial surface integrals are taken only over the single cell faces specified by the $x_i = \pm L/2$ conditions. Note that for each of the two Cartesian directions in Fig. 4 ($i = 1,2$) the $d\mathbf{S}$ elements point in opposite directions. Since the diffusive current $\mathbf{j}$ represents the full current on the reservoir boundaries, the entropy production of Eq. (41) is then

$$\int d^3x\, \sigma = -k_B \sum_{i=1}^{4} \dot{N}_i \left[\ln\, \rho_0 + \ln\left(1 + \frac{\Delta C_i}{2\rho_0}\right)\right], \tag{43}$$

where we have used the reservoir boundary conditions for ρ given in Fig. 4.

We can connect these definitions of the $\dot{N}_i$ to the porous-continuum transport current of Eq. (38) as

$$\Delta\dot{N}_i \equiv \frac{\dot{N}_{i+2} - \dot{N}_i}{2} = A J_i, \tag{44}$$

where A is the area of a face of the central cell. Expanding $\ln(1+x) \approx x$ and noting that particle conservation in the steady state requires $\sum_{i=1}^{4} \dot{N}_i = 0$, we obtain the entropy production as

$$\int d^3x\, \sigma = k_B \sum_{i=1}^{2} \Delta\dot{N}_i \frac{\Delta C_i}{\rho_0}, \tag{45}$$

where we also have used that $\Delta C_{i+2} = -\Delta C_i$. This is the exact same expression as can be obtained from the Clausius relation given earlier

$$\int d^3x\, \sigma = \sum_{i=1}^{4} \frac{dS_i}{dt} = \sum_{i=1}^{4} -\frac{\mu_i}{T}\dot{N}_i, \tag{46}$$

where S_i and μ_i are entropies and chemical potentials in the reservoir cells i. Using Eq. (35) for μ_i/T and the same expansion $\ln(1+x) \approx x$, Eq. (46) becomes Eq. (45), which is a consistency test of the formalism.

Finally, the entropy production can be written in terms of fluxes $\dot{x}_i$ and forces F_i. The entropy production of the total system, including both the central cell and the reservoirs, is

$$\dot{S}_{\rm tot} = \int d^3x\, \sigma = \sum_{i=1}^{2} \frac{\partial S_{\rm tot}}{\partial x_i}\dot{x}_i = \sum_{i=1}^{2} \dot{x}_i F_i, \tag{47}$$

where comparison with Eq. (45) shows that

$$x_i = \Delta N_i, \tag{48}$$

$$F_i = k_B \frac{\Delta C_i}{\rho_0}. \tag{49}$$

These are the results needed to apply the Onsager theory.

B. The linear laws and the reciprocity relations

In order to obtain the desired reciprocity relations the final step is to obtain the linear laws expressing the decay of the $\dot{x}_i$'s in terms of the F_i's. It follows from Eq. (16) that the average,

$$\langle x_i F_j \rangle_{\mathbf{u}} = -k_B \delta_{ij}, \tag{50}$$

where k_B is Boltzmann's constant. This result comes from a partial integration using the distribution in Eq. (16), see Ref. [19]. Following standard procedures [4] we argue as follows: In a steady state where averages no longer change, there are still stationary nonzero values for $\langle \Delta N_i \rangle_{\mathbf{u}}$. In the following we perform the replacement:

$$\Delta N_i \to \Delta N_i - \langle \Delta N_i \rangle_{\mathbf{u}}, \tag{51}$$

where for simplicity, we keep the notation ΔN_i so that now

$$\langle \Delta N_i \rangle_{\mathbf{u}} = \langle \Delta N_i \rangle_{-\mathbf{u}} = 0. \tag{52}$$

Since the new variables ΔN_i are just as much functions of $\{\mathbf{r}_k(t)\}_{\mathbf{u}}$ as the N_i's, the basic time-reversal symmetry holds for the new variables too, and we may write

$$\langle \Delta N_j(\tau) \Delta N_k(0) \rangle_{\mathbf{u}} = \langle \Delta N_j(-\tau) \Delta N_k(0) \rangle_{-\mathbf{u}}. \tag{53}$$

Now, time translational invariance of an equilibrium average implies that Eq. (53) may be written

$$\langle \Delta N_j(\tau) \Delta N_k(0) \rangle_{\mathbf{u}} = \langle \Delta N_j(0) \Delta N_k(\tau) \rangle_{-\mathbf{u}}. \tag{54}$$

Subtracting the $\tau = 0$ version of the above equation from Eq. (53), dividing by τ, and taking the $\tau \to 0$ limit gives

$$\langle \Delta \dot{N}_j \Delta N_k \rangle_{\mathbf{u}} = \langle \Delta \dot{N}_k \Delta N_j \rangle_{-\mathbf{u}}. \tag{55}$$

We now only need to insert the linear laws governing the $\dot{N}_i$'s in terms of the F_i's to obtain the corresponding reciprocity relations. Note that the force F_i can be written in terms of the macroscopic gradient in particle density as $(\nabla \rho_0)_i = \rho_0 F_i/(k_B L)$ so that the linear laws may be obtained directly from Eq. (38) as

$$\Delta \dot{N}_i = A\left(\rho_o \overline{\mathbf{U}} - D_{ij} \frac{\rho_0}{k_B L} F_j\right). \tag{56}$$

Inserting this in Eq. (55) gives

$$\left\langle \left(\rho_0 \overline{U}_j - \frac{\rho_0}{k_B L} D_{ji}(\mathbf{u}) F_i\right) x_k \right\rangle_{\mathbf{u}} = \left\langle \left(-\rho_0 \overline{U}_k - \frac{\rho_0}{k_B L} D_{ki}(-\mathbf{u}) F_i\right) x_j \right\rangle_{-\mathbf{u}}. \tag{57}$$

Then, using Eqs. (50) and (52) we are left with

$$D_{jk}(\mathbf{u}) = D_{kj}(-\mathbf{u}). \tag{58}$$

This is the symmetry suggested by Auriault *et al.* [9] to hold in the small Péclet number limit. It is proven here to hold on the basis of a modified Onsager theory for any values of the Péclet number.

VI. CONCLUSIONS

To summarize, we have shown that a mesoscopic description suffices as a basis for Onsager reciprocity, in particular, for the case of hydrodynamic dispersion. But the theory is directly applicable to other stochastic descriptions with time-reversal invariance as well: If the particles were taken to represent a temperature rather than a concentration field, heat conduction in the solid matrix could be represented by letting the particles pass through the solid boundaries of the porous medium, and a different $p(\delta \mathbf{v})$ distribution could be applied inside the solid. If it were still symmetric, similar reciprocity relations would hold. It would also be straightforward to include reversible chemical reactions between different species of particles.

Since it is also possible to obtain the symmetry relation of Eq. (58) for arbitrary Pe numbers on the basis of the pore-level advection-diffusion equation [18], the present statistical mechanical treatment is not the only route to the result. In this respect our treatment resembles that of anisotropic heat conduction where the symmetries were also largely known beforehand. Rather, the main interest of the result lies in the conceptual basis for the Onsager theory, which, in particular opens a route to study processes where a hydrodynamic velocity field may be assumed as a steady state background.

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